

CERTIFICATION REPORT

Certification of the mass concentrations of calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium and of pH and conductivity in groundwater

Certified Reference Material ERM[®]-CA616

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Certified Reference Material ERM[®]-CA616

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Summary

This report presents the preparation and certification of the groundwater certified reference material ERM-CA616. All the steps required for the production of this water-matrix certified reference material are described in detail, from the sampling of natural groundwater until the characterisation exercise that lead to the final assignment of the certified values, following ISO Guide 34:2009 [1] and ISO Guide 35:2006 [2].

Homogeneity and stability of the water material were investigated with dedicated studies and the certification campaign for the material characterisation was based on an inter-comparison among several experienced laboratories. IRMM organised and coordinated all the phases of this project and carried out the evaluation of data.

The certified values were calculated as the unweighted mean of the laboratory means of the accepted sets of results for each parameter, see below. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) [3]. The stated expanded uncertainties include contributions from characterisation, homogeneity and stability.

GROUNDWATER		
	Mass Concentration	
	Certified value ¹⁾ [mg/L]	Uncertainty ²⁾ [mg/L]
Calcium	42.6	1.4
Chloride	44.6	0.9
Magnesium	10.1	0.3
<i>Ortho</i> -phosphate	2.24	0.10
Potassium	5.79	0.15
Sodium	27.9	0.8
	Electrochemical property	
	Certified value ¹⁾ [μS/cm]	Uncertainty ²⁾ [μS/cm]
Conductivity (20 °C)	426	5
	Chemical property	
	Certified value ¹⁾	Uncertainty ²⁾
pH (20 °C)	7.12	0.18
<small>1) Unweighted mean value of the means of accepted sets of data each set being obtained in a different laboratory and/or with a different method of determination. The certified values and their uncertainties are traceable to the International System of Units (SI). 2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) with a coverage factor $k = 2$, corresponding to a level of confidence of about 95 %.</small>		

Table of Contents

1. Introduction.....	4
2. Participants.....	5
3. Time schedule	7
4. Sampling of the material	7
5. Processing of the material	7
5.1 Preparation steps	7
5.2 Spiking, homogenisation and ampouling.....	8
5.3 Sterilisation	8
6. Homogeneity study.....	9
7. Minimum sample intake	12
8. Stability studies	12
8.1 Set-up of stability studies.....	12
8.2 Results of stability studies	13
9. Characterisation.....	16
9.1 Study design.....	16
9.2 Data evaluation and results.....	17
10 Certified values and uncertainties	21
11 Additional material information.....	23
12 Metrological traceability	23
13 Commutability.....	23
14 Instructions for use	24
14.1 Storage conditions.....	24
14.2 Minimum sample intake.....	24
14.3 Safety precautions	24
14.4 Intended use.....	24
14.5 Use of the certified value.....	24
References.....	25
Acknowledgments	26
Annex 1a	27
Annex 1b	28
Annex 2	29
Annex 3	31
Annex 4	47
Annex 5	55

Glossary

ANOVA	analysis of variance
α	significance level
BCR	Community Bureau of Reference
CFA	continuous flow analysis
CRM	certified reference material
ERM	European Reference Material
DT	double Grubbs test
Δ_m	absolute difference between mean measured value and certified value
F-AAS	flame atomic absorption spectrometry
IC-/CD	ion chromatography with conductimetric detection
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
IRMM	Institute for Reference Materials and Measurements
ISO	International Organization for Standardization
k	coverage factor
MS_{between}	mean square between-bottle from ANOVA
MS_{within}	mean square within-bottle from ANOVA
n	number of replicates per bottle
OVAM	Openbare Vlaamse Afvalstoffenmaatschappij
PTFE	polytetrafluoroethylene
QC	quality control
RSD	relative standard deviation
RSE	relative standard error ($=RSD/\sqrt{n}$)
s	standard deviation
s_{bb}	between-bottle standard deviation
SFA	segmented flow analysis
SI	International System of Units
PHOT	spectrophotometry
ST	single Grubbs test
s_{wb}	within-bottle standard deviation
$t_{\alpha,df}$	critical t -value for a t -test, with a level of confidence equal to $1-\alpha$ and df degrees of freedom
t_{sl}	shelf life
u_{bb}	standard uncertainty related to possible between-bottle heterogeneity
u_{bb}^*	standard uncertainty of heterogeneity that can be hidden by method repeatability
u_{Δ}	combined standard uncertainty of measurement result and certified value
u_{char}	standard uncertainty related to characterisation
u_{CRM}	combined standard uncertainty of a certified value
U_{CRM}	expanded uncertainty of a certified value
u_{ITS}	standard uncertainty related to long-term stability
u_m	standard uncertainty of a measurement result
u_{rect}	standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution
VMM	Vlaamse Milieumaatschappij
x_i	time point of a stability study
\bar{x}	average of all time points of a stability study
\bar{y}	average of all results of the homogeneity study

1. Introduction

Groundwater is one of the most important natural resources. It is a crucial source of drinking water, supplying the water systems for about two-thirds of European Union citizens: its safety is therefore vital.

The legislative framework for its effective protection is established by the Water Framework Directive (WFD, 2000/60/EC) [4] which addresses inland surface waters, transitional waters, coastal waters and groundwater.

A Groundwater "daughter" Directive (2006/118/EC) [5] was adopted (12th December 2006) by the European Parliament and Council on the protection of groundwater against pollution and deterioration, strengthening the existing Groundwater Directive (80/68/EEC) [6] to be repealed in 2013.

This new directive establishes a regime which sets groundwater quality standards and introduces measures to prevent or limit inputs of pollutants into groundwater, including criteria for the identification and reversal of significant and sustained upward trends in pollutant concentrations.

The compliance of the groundwater with good chemical status criteria is also based on threshold values established by Member States for, among others, arsenic, cadmium, lead, mercury, ammonium, chloride, sulfate and conductivity.

On the other hand, the WFD recognises the importance of the cycle linking groundwater and surface waters and it specifies that good status - in both quantity and chemical terms - of a groundwater body also means protecting the surface water bodies and terrestrial ecosystems that depend on its waters.

The WFD requires the establishment of monitoring programmes covering groundwater quantitative status, chemical status and the assessment of significant, long-term pollutant trends resulting from human activity. The confidence in any assessment of groundwater will depend on the quality in the context of measurement data. A continuous quality assurance system should be therefore developed and implemented for each monitoring institution to ensure that the reported results meet assured target levels of precision and bias [7].

The availability of appropriate certified reference materials will be an asset in the validation of analytical methods, ensuring accuracy and traceability of the measurement results [8].

The European Commission's Community Bureau of Reference (BCR) issued two artificial groundwater CRMs (CRM-616 and 617) in 1998. ERM-CA616, the production of which was carried out by IRMM and is described in the present report, is intended to be the replacement

for these two materials and to be used as quality assurance and quality control tool by the laboratories involved in the mandatory monitoring prescribed under the WFD.

General information

The parameters certified in ERM-CA616 are commonly referred to as major components or major elements of the water and are the following: calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium. The properties conductivity and pH are also certified. Ammonium values are given as additional material information.

The certified values are stated as mass concentrations, milligrams per liter (mg/L) because this is the most common way used by the "water analysis" community to express concentration of a substance in water. Conductivity value is expressed in $\mu\text{S}/\text{cm}$ while for pH value no unit is applicable.

2. Participants

- Sampling and processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34, BELAC No 268-TEST)

- Homogeneity study

IWW Rheinisch-Westfälisches Institut für Wasser, Mülheim an der Ruhr, DE
(accredited to ISO/IEC 17025 for chemical analysis of groundwater, DGA DAC-PL-0170-02-01)

- Stability studies (in alphabetical order)

DVGW-Technologiezentrum Wasser, Karlsruhe, DE
(accredited to ISO/IEC 17025 for measurements of chemical parameters in groundwater, DACH DAC-PL-0142 -01-10)

IWW Rheinisch-Westfälisches Institut für Wasser, Mülheim an der Ruhr, DE
(accredited to ISO/IEC 17025 for chemical analysis of groundwater, DGA DAC-PL-0170-02-01)

- Characterisation analyses (in alphabetical order)

ALS Czech Republic s.r.o., Praha, CZ
(accredited to ISO/IEC 17025 for chemical analysis of water, CAI No 521/2008)

Bayer Antwerpen NV, Centraal Laboratorium, Antwerpen, BE
(accredited to ISO/IEC 17025 for chemical analysis of water, BELAC No 264-TEST)

Chemservice SRL, Novate Milanese, IT
(accredited to ISO/IEC 17025 for chemical analysis of groundwater, SINAL No 0004)

Consiglio Nazionale delle Ricerche, Istituto per lo Studio degli Ecosistemi, Verbania
Pallanza, IT

DVGW-Technologiezentrum Wasser, Karlsruhe, DE
(accredited to ISO/IEC 17025 for measurements of chemical parameters in groundwater, DACH
DAC-PL-0142 -01-10)

EPAL- Empresa Portuguesa das Águas Livres, S.A - LABORATÓRIO CENTRAL,
Lisboa, PT
(accredited to ISO/IEC 17025 for measurements of chemical parameters in drinking water, IPAC
No L0242)

IWW Rheinisch-Westfälisches Institut für Wasser, Mülheim an der Ruhr, DE
(accredited to ISO/IEC 17025 for chemical analysis of groundwater, DGA DAC-PL-0170-02-01)

Laboratoire National de métrologie et d'essais, LNE, Paris, FR
(accredited to ISO/IEC 17025 for measurement of pH in reference standard solutions, Cofrac, No
2-54)

Macaulay Land Use Research Institute, Aberdeen, UK
(accredited to ISO/IEC 17025 for chemical parameters in natural waters, UKAS No 1917)

Rijkswaterstaat, Ministerie van Verkeer and Waterstaat, Waterdienst, Lelystad, NL
(accredited to ISO/IEC 17025 for chemical analysis of surface and wastewater, RvA, No L194)

VA SYD, Malmö, SE
(accredited to ISO/IEC 17025 for chemical analysis of freshwater, SWEDAC No 07-213-51.1056)

Vlaamse Instelling voor Technologisch Onderzoek - VITO, Mol, BE
(accredited to ISO/IEC 17025 for chemical analysis of groundwater, BELAC No 045-TEST)

Vlaamse Milieumaatschappij (VMM), Afdeling Rapportering Water, Dienst
Laboratorium, BE
(accredited to ISO/IEC 17025 for chemical analysis of surface and wastewater, BELAC No 163-
TEST)

- Project management and data evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and
Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34, BELAC No 268-TEST)

3. Time schedule

Sampling	April 2007
Processing	September 2007
Homogeneity and short-term stability measurements	July 2008
Long-term stability measurements	December 2009
Characterisation measurements	February 2009

4. Sampling of the material

The site chosen for the sampling of groundwater was a locked well located in Maaseik, North-East Limburg, Belgium. The place was carefully selected (with respect to water composition and discharge) through the Databank Ondergrond Vlaanderen, a database containing information on all the wells belonging to the Flemish groundwater monitoring network, under the responsibility of the water division of Vlaamse Milieumaatschappij (VMM).

The sampling was carried out by an IRMM team with the logistical support and under the supervision of representatives from the water division of VMM. The protocol of good water sampling as laid down by the Openbare Vlaamse Afvalstoffenmaatschappij (OVAM, Public Waste Agency of Flanders) was followed.

One polyethylene pre-cleaned drum of 200 L was filled with the aid of a frequency-regulated Grundfos pump. The PTFE tubes and the in-line filter (Versaflow™ Capsule containing a 0.45 µm Versapor® Membrane with pre-filter 8 µm PN 12131, Pall Corp, Port Washington, NY, US) were extensively flushed to avoid external contamination before starting with the water collection into the drum. The sampling depth was about 7 meters and the water was collected with a speed of about 10 L/min. The drum was then stored at +4 °C at IRMM premises until further processing took place.

5. Processing of the material

5.1 Preparation steps

From the initial container, the bulk water was pumped via an in-line filter (AcroPack™ 1000, Supor® Membrane 0.8/0.2 µm Pall Corp, Port Washington, NY, US, offering also bacterial retention,) to another pre-cleaned drum of 200 L. The drum, the PTFE paddle used for homogenisation and the PTFE tubes used for transferring the water were all previously washed with ~2 % v/v HNO₃ and subsequently extensively rinsed with de-ionised water (18.2

µS/cm). For cleaning of the drum, a Turbula mixer (Turbula T-200, W.A.B, Basel, CH) was employed. The tubes and filter were also "conditioned" with the groundwater for few minutes, before starting the collection into the second drum intended to be used for spiking and homogenisation of the bulk water.

The borosilicate hand-made ampoules of 100 mL were rinsed one by one with de-ionised water and dried at 60 °C in a drying cabinet (Elbanton, Kerkdriel, NL). After drying, and before being used, they were sealed with Parafilm to avoid deposition of dust.

5.2 Spiking, homogenisation and ampouling

A preliminary characterisation of the water, with regard to the parameters to be certified, was performed to find out if it was necessary to spike any parameter to reach the target levels. Following these analyses, a spiking with a freshly prepared solution of $\text{NH}_4\text{H}_2\text{PO}_4$ 99.999 % (Sigma-Aldrich Chemie, Steinheim, DE) in ultra-pure water (18.2 µS/cm) was performed to increase the concentration of ammonium and *ortho*-phosphate to 0.4 mg/L and 2.2 mg/L, respectively. After spiking, that was performed after filtration of the water (see Section. 5.1), homogenisation was achieved by continuous stirring with a PTFE paddle for about two hours. Quantities of about 97 mL of water were subsequently filled into 100 mL borosilicate glass ampoules. The head-space was flushed with argon before flame-sealing, using an automatic ampouling machine (ROTA R910/PA, Wehr/Baden, DE).

5.3 Sterilisation

Before thermal sterilisation of the CRM-batch several tests had been performed by autoclavation of sealed ampoules. This was done to evaluate the feasibility of this conservation method with respect to sterilisation efficiency and risk of glass breakage. To ensure that the sterilisation process had effectively taken place, 3 ampoules from a batch of 90 were spiked with *Escherichia Coli* (200 CFU/µL). To double-check, a biological indicator (3M Attest Biological Indicator 1262/1262P using *Bacillus stearothermophilus* ATCC 7953) was also taped on one of the ampoules. After autoclavation, the spiked water and the indicator were incubated (together with positive and negative controls). The autoclaved and spiked waters were found sterile, thereby confirming the efficiency of the sterilisation process.

On the basis of these tests, the water in the closed ampoules of candidate certified reference material ERM-CA616 was sterilised by autoclavation at 121 °C for 15 min (Webeco, Ober-Ramstadt, DE). In total 3 % of the ampoules broke during the sterilisation process.

Subsequently, labelling of 1720 units took place. After this step, the ampoules were stored at 18 °C in the dark.

6. Homogeneity study

To check the homogeneity of the material with regard to the parameters to be certified, 24 units were chosen using a random stratified sample picking scheme. The number of units is based on the produced batch size (approximately corresponding to the cubic root of the total number of units). The batch is divided into the same number of groups and one unit is picked from each group. These samples were analysed in duplicate for content of ammonium, calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium (12 ampoules) and for pH and conductivity at 20 °C (12 ampoules).

The measurements were performed under repeatability conditions, i.e. during one analytical run, using validated methods and according to an imposed random sequence to permit distinction between possible trends in the analytical sequence and in the filling order. Quality control (QC) samples and blank samples were analysed at the beginning, at the end and at various points within the sequence.

Ammonium and *ortho*-phosphate were measured by photometry, calcium, magnesium, potassium and sodium by inductively coupled plasma optical emission spectrometry (ICP-OES), chloride by ion chromatography with conductimetric detection (IC-CD), pH by potentiometry and conductivity by conductimetry, both reported at 20 °C. Sample intakes ranged from 0.1 mL to 25 mL, depending on the analyte and on the technique.

The 24 results of each analyte were evaluated by one-way analysis of variance (ANOVA). The unimodal distribution of data is an important prerequisite in order to apply the ANOVA statistical evaluation, therefore the distributions of sample averages as well as individual results were checked both for normality employing normal probability plots and for unimodality using histograms. For all analytes, the individual results and ampoule averages followed an approximately normal and unimodal distribution, with the exception of the individual values for calcium and magnesium, for which a bimodal distribution could be observed. This minor deviation from unimodality does not significantly affect the estimate of the between-unit standard deviation.

Data were checked for presence of trends and outliers.

For *ortho*-phosphate, trends were found both in the filling (toward lower values) and in the analytical sequence (towards higher values). For ammonium a trend towards lower values was

observed in the filling sequence, while for calcium, magnesium and pH a trend in the analytical sequence was present (all trends were towards higher values and both at 95 and 99 % confidence level).

Results were corrected for their trend in the analytical sequence if the trend was significant on at least a 95 % confidence level as shown below:

$$\text{corrected result} = \text{measured result} - (b \cdot i) \quad (1)$$

b = slope of the linear regression

i = position of the result in the analytical sequence

After correction of the trend in the analytical sequence, for calcium a trend in the filling sequence towards higher values became apparent, at 95 % confidence level.

Two outlying individual results (1st replicates of bottles 593 and 985, Grubbs double test at $\alpha=0.05$) were found for chloride and two outlying sample averages (units 985 and 1277, Grubbs double test at $\alpha=0.05$) were found for potassium.

Since no technical reasons were detected for the outlying results, all data were retained for statistical analysis.

In the case of presence of trends and/or of outlier averages, the evaluation by ANOVA could be not the most appropriate one and therefore an alternative approach for the estimation of the heterogeneity was followed (see formula 5 below).

The ANOVA allowed the calculation of the within- (s_{wb}) and between-unit homogeneity (s_{bb}), estimated as standard deviations, according to the following formulas:

$$s_{wb} = \sqrt{MS_{within}} \quad (2)$$

MS_{within} = mean squares within-ampoule

s_{wb} is equivalent to the s of the method, provided that subsamples are representative for the whole bottle.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (3)$$

$MS_{between}$ = mean squares between-ampoule

n = number of replicates per ampoule.

When MS_{between} is smaller than MS_{within} , s_{bb} can not be calculated. Instead, u^*_{bb} , the heterogeneity that can be hidden by the method repeatability, is calculated, according to the following expression [9]:

$$u^*_{\text{bb}} = \frac{s_{\text{wb}}}{\sqrt{n}} \sqrt{\frac{2}{v_{MS_{\text{within}}}}} \quad (4)$$

$v_{MS_{\text{within}}} = \text{degrees of freedom of } MS_{\text{within}}$

For potassium, for which outlying bottle means were detected, an alternative estimate of heterogeneity was calculated. Between-bottle heterogeneity was modelled as rectangular distribution limited by the most extreme outlying average. The standard uncertainty using these outliers (u_{rect}) was then estimated as

$$u_{\text{rect}} = \frac{|\text{largest outlier} - \bar{y}|}{\sqrt{3}} \quad (5)$$

$\bar{y} = \text{average of all results}$

A similar approach was used for ammonium and *ortho*-phosphate, where a trend in the filling sequence was detected and for calcium for which a filling trend became apparent after correction of the analytical sequence trend. Here, u_{rect} was estimated using the half-width of a rectangular distribution between the highest and lowest bottle average:

$$u_{\text{rect}} = \frac{|\text{highest result} - \text{lowest result}|}{2 \cdot \sqrt{3}} \quad (6)$$

For the parameters for which ANOVA was applied, the larger value between s_{bb} and u^*_{bb} is taken as uncertainty contribution for homogeneity, u_{bb} . u_{rect} will be taken as u_{bb} for potassium, ammonium, *ortho*-phosphate and calcium (Table 1).

Even with retention of outliers, the between-unit variation is generally low (well below 2 %). All homogeneity data can be found in Annex 1a and 1b.

Table 1. Results of the homogeneity study

	Mean value	unit	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u_{bb,rel}^*$ [%]	$u_{rect,rel}$ [%]	$u_{bb,rel}$ [%]
ammonium	0.415	mg/L	-	-	-	1.6	1.6
calcium	39.83	mg/L	-	-	-	0.2	0.2
chloride	44.69	mg/L	0.2	$MS_{between} < MS_{within}$	0.1	-	0.1
magnesium	9.848	mg/L	0.2	0.2	0.1	-	0.2
<i>ortho</i> -phosphate	2.284	mg/L	-	-	-	1.2	1.2
potassium	5.536	mg/L	-	-	-	0.7	0.7
sodium	27.194	mg/L	0.3	0.3	0.2	-	0.3
pH (20 °C)	6.85	-	0.4	0.6	0.2	-	0.6
conductivity (20 °C)	426	μS/cm	0.1	0.1	0.0	-	0.1

7. Minimum sample intake

The establishment of the minimum sample intake, *i.e.* the minimum subsample representative of the whole ampoule, was not specifically addressed due to the nature of the material itself (water). The heterogeneity of solutions is known to be very small or even negligible.

Nevertheless, minimum sample intake is defined as the smallest amount of sample for which homogeneity has been demonstrated through the obtainment of a technically valid set of results accepted for the characterisation. These amounts are the following: 0.005 mL for chloride, 0.1 mL for *ortho*-phosphate, 0.5 mL for calcium, magnesium and sodium, 2 mL for potassium and 10 mL for pH and conductivity.

8. Stability studies

8.1 Set-up of stability studies

Stability studies are conducted to establish both dispatch conditions (short-term stability) as well as storage conditions (long-term stability).

Principal means of stabilization of the water for long-term perspective were the creation of an inert atmosphere by flushing argon within the ampoule just before filling and the sterilization by exposing the ampoules to an autoclaving process (see 5.3).

For performing the stability studies according to the planned tested temperatures and time points, 28 ampoules were required for the short-term stability (14 for pH and conductivity and 14 for the rest of parameters) and 16 ampoules were required for each of the long-term

stability schemes, see below (8 for pH and conductivity and 8 for the rest of parameters), selected by random stratified sampling from the entire batch produced.

The set-up of the studies followed an isochronous scheme [10] as described below:

- Short-term stability

Two ampoules were kept at +18 °C and +60 °C for 1, 2 and 4 weeks, respectively after which they were put at +4 °C, the temperature at which the "reference" ampoules were stored. Two replicate analyses per ampoule were performed under repeatability conditions *i.e.*, all analyses were included in the same analytical run according to a prescribed randomly selected sequence.

- Long-term stability

Two ampoules were kept at +18 °C for 4, 8, and 12 months, respectively (1st scheme) and for 8, 16 and 24 months, respectively (2nd scheme). The reference temperature was +4 °C. Three replicates per ampoule were performed under repeatability conditions.

The measurements were performed by photometry for ammonium and *ortho*-phosphate, by ICP-OES for calcium, magnesium, potassium and sodium, by IC-CD for chloride, by potentiometry for pH and by conductimetry for conductivity (results reported at 20 °C), using standardised and in-house validated methods.

8.2 Results of stability studies

The results were grouped and evaluated for each time point and temperature. Results were screened for single and double outliers by applying the Grubbs test at confidence levels of 95 % and 99 %, respectively. Data were plotted against time and the regression lines were calculated to check for significant trends possibly indicating degradation of the material. The observed slopes were tested for significance using a *t*-test, with $t_{\alpha,df}$ being the critical *t*-value (two-tailed) for a significance level $\alpha = 0.05$ (95 % confidence interval).

The results for the short-term stability at +18 °C and +60 °C are summarised in Table 2.

Outliers were detected at 18 °C and/or at 60 °C for almost all the parameters (except *ortho*-phosphate, pH and conductivity). These were mostly individual results; in case of ammonium at 60 °C, however, both replicates of ampoule 1119 were flagged as outliers. No technical reason for exclusion of the outliers could be found, therefore they were retained leading to a conservative estimate of the short-term stability uncertainty.

Table 2. Short-term stability

	18 °C			60 °C		
	outliers	slope significance	$u_{\text{sts,rel}}[\%]$ /week	outliers	slope significance	$u_{\text{sts,rel}}[\%]$ /week
ammonium	-	no	0.2	unit 1119 (DT, 95 %)	no	0.2
calcium	One (ST, 95 and 99 %)	no	0.1	One (ST, 95 %)	no	0.1
chloride	One (ST, 95 and 99 %)	no	0	Two (DT, 95 %)	no	0
magnesium	-	no	0	One (ST, 95 and 99 %)	no	0.1
ortho-phosphate	-	no	0.2	-	no	0.3
potassium	-	no	0.1	One (ST, 95 %)	no	0.2
sodium	-	no	0.1	One (ST, 95 %)	no	0.2
pH (20 °C)	-	no	0.1	-	no	0
conductivity (20 °C)	-	no	0	-	Yes (95 %)	0.1*

* including trend (u_{sts} includes additional contribution given by the slope of the regression line)

ST = single Grubbs test

DT = double Grubbs test

The resulting uncertainty contributions for short-term stability were calculated according to Linsinger *et al.* [11] and were negligible for all analytes (max 0.3 % for one week at 60 °C). Because the potential degradation due to dispatch can be considered negligible if compared to the uncertainty of the final certified value, the uncertainty contribution from the short-term stability will not be considered in the final uncertainty budget.

A significant slope was observed for the conductivity results at 60 °C at 95 % confidence interval, therefore in order to avoid any possible degradation, it was decided that the transport of the material will occur under cooled conditions.

The results of the two long-term stability studies at +18 °C (1st scheme lasting 12 months and 2nd scheme lasting 24 months) were combined and evaluated together to obtain more confidence about the assessment of the stability, with the exception of pH for which only the 2-years study measurements were used (see below for more details).

Since the two datasets were obtained from different laboratories and at different points in time, a correction had to be applied. For all parameters, the correction factor was between 0.99 and 1.05. The results are summarised in Table 3 (graphical depictions of the data can be found in Annex 2). The uncertainty due to storage at 18 °C is estimated for a shelf-life of 2

years (with exception of ammonium for which is calculated for 4 years including trend as a significant slope was observed in this case).

The uncertainty of stability u_{lts} of the materials was calculated as uncertainty of the slope of the regression line multiplied with the chosen shelf life [11]:

$$u_{lts} = \frac{s}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl} \quad (7)$$

with s being the standard deviation of all 48 individual results of the stability studies (with the exception of pH for which only the 24 independent measurements of the 2nd scheme were used), x_i being the time point for each replicate, \bar{x} being the average of all time points and t_{sl} being the pre-defined shelf life (24 months with the exception of ammonium for which 48 months was chosen).

Table 3. Long-term stability

	18 °C		
	outliers	slope significance	$u_{lts,rel}$ [%] (2 years)
ammonium	One (ST, 95 %)	Yes (95 %)	1.7*
calcium	-	no	0.4
chloride	One (ST, 95 and 99 %)	no	0.2
magnesium	-	no	0.4
<i>ortho</i> -phosphate	One (ST, 95 and 99 %)	no	1.0
potassium	One (ST, 95 %)	no	0.4
sodium	-	no	0.3
pH (20 °C)	-	no	0.2**
conductivity (20 °C)	-	no	0.1

*calculated for 4 years, including trend (u_{lts} includes additional contribution given by the slope of the regression line)

**estimation using only the 2 years long term stability data

ST = single Grubbs test

The outliers detected for ammonium, chloride, *ortho*-phosphate and potassium, were kept for the statistical evaluation, in absence of any technical reason justifying their rejection. A

tentative removal of these outliers did not result in a significant trend of the data, which means that the estimate of u_{ls} is conservative.

A significant negative trend was observed only at 95 % significance level for ammonium. The removal of the outlying value for ammonium would result in the loss of the trend observed for this parameter, casting doubts on the actual occurrence of this trend, but in absence of other data, no other conclusions can be drawn.

For pH the u_{ls} was estimated using only the measurements of the long term stability 2nd scheme lasting 2 years. The reason for it relies on the fact that some doubts arose concerning the validity of the data of the 1st scheme, underpinned by the failure of the concerned laboratory in measuring pH in the QC samples sent during a simultaneous certification campaign for another CRM (ERM-CA408, simulated rainwater).

For all the analytes, the standard uncertainty introduced by the long-term stability at +18 °C (recommended storage temperature of the material) for 2 years is $\leq 1.0 \%$ (with the exception of ammonium, which value will anyway not be certified see Section 11 Additional Material Information).

u_{ls} is included as one of the contribution to the final uncertainty budget of the certified value. The shelf life of the material will be re-evaluated in the future, based on the results of regular stability monitoring carried out after certification and release of the material.

9. Characterisation

9.1 Study design

The characterisation of the material was carried out by an intercomparison exercise and finalised in 2009. Laboratories were selected on the basis of expertise in water analysis (with supporting documentation on their measurement capabilities), quality requirements criteria (e.g. successful participation in intercomparisons in the relevant field and/or previous characterisation exercises), with accreditation for the specific analysis to be performed considered as an asset. Laboratories were only allowed to use validated methods.

Most participating laboratories were accredited to ISO 17025, and where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (see Section 2).

In order to prevent biased results, a number of precautionary measures were taken:

- when possible, completely different and independent analytical methodologies were chosen for the determination of the same parameter (aiming to at least 2 laboratories per method), thus being able to demonstrate the absence of method bias.
- six independent measurements per laboratory were required, meaning that a new sample preparation had to be performed for each measurement. These measurements were prescribed to be spread over two days, to ensure within-laboratory reproducibility conditions.
- to further demonstrate the accuracy and traceability of their data, laboratories were asked to report results of quality control samples analysed together with the characterization samples and were asked to insert blanks in the measuring sequence.
- samples for the characterisation study covered the whole batch produced and were selected using a random stratified sampling scheme.

The two quality control samples received by the laboratories were the certified reference materials BCR-616 (re-labelled as QC1) and BCR-617 (re-labelled as QC2), "Artificial groundwater (high carbonate level)" and "Artificial groundwater (low carbonate level)", respectively.

Laboratories were also asked to provide an estimate of their measurement uncertainty and to describe the approach used to derive the uncertainty budget.

Depending on the methodology employed (and the relative sample intake), laboratories received 6 (3 for pH and conductivity measurements and 3 for the rest of analytes) or 4 (2 for pH and conductivity measurements and 2 for the rest of analytes) ampoules of candidate certified reference material ERM-CA616: six independent results were to be returned. Additionally they received two ampoules of quality control samples, as explained before; only two replicates were asked in this case (only 1 measurement was required for pH and conductivity due to the relatively large sample intake needed for these measurements and the limited sample volume, around 75 mL).

For helping the laboratories in establishing the correct calibration curve, in the guidelines for characterisation measurements an approximate concentration range for the parameters to be analysed was provided.

9.2 Data evaluation and results

A detailed overview of the analytical techniques used by the laboratories for the characterisation of ERM-CA616 is presented in Annex 3, listed per parameter.

Upon receipt of the datasets, the results were subject to technical evaluation. The results of the QC samples could be directly used to check for absence of significant bias.

Datasets were rejected whenever the laboratory reported a technical problem and when one or both quality control samples results did not agree with the certified values (according to ERM Application Note 1 [12]). A summary of the data evaluation is presented in Table 4.

The following datasets were discarded:

L2: measurement results of potassium rejected because the result from QC2 did not agree with the certified value.

L3: measurement results of chloride rejected because the result from QC1 did not agree with the certified value; measurements of *ortho*-phosphate excluded because the laboratory determined total phosphorus.

L4: measurement results of pH and conductivity were discarded as a consequence of reported problems with the washing of the electrodes between replicates (the three results were obtained from the same aliquot of water, not in compliance with the guidelines requesting for three independent measurements)

L11: measurement results of chloride were rejected because the result from QC2 did not agree with the certified value.

A close look to the results for ammonium revealed that the two laboratories using IC delivered consistently higher results than all the other laboratories, all using spectrophotometric methods. It was decided to keep the ammonium datasets obtained by spectrophotometry for further statistical assessment while the two IC datasets are excluded from statistical analysis.

After this technical scrutiny, all the remaining datasets were accepted for further statistical assessment. Twelve datasets were accepted for ammonium, calcium, magnesium, sodium, pH and conductivity, 11 datasets were accepted for potassium and *ortho*-phosphate and 10 datasets were accepted for chloride.

Table 4. Summary of the technical evaluation

	ammonium	calcium	chloride	magnesium	<i>ortho</i> -phosphate	potassium	sodium	pH	conductivity
L0									
L1									
L2						Discarded QC2 out			
L3			Discarded QC1 out		Discarded Determination of total P				
L4								Discarded Reported problems in washing the electrodes, 3 consecutive measurements on the same aliquot	Discarded Reported problems in washing the electrodes, 3 consecutive measurements on the same aliquot
L5									
L6									
L7	-	-	-	-	-	-	-		
L8									
L9									
L10									
L11			Discarded QC2 out						
L12									

- parameter not analysed

The datasets accepted on technical grounds were tested for outlying laboratories using Dixon, Grubbs and Nalimov *t*-test, for normality of means distribution using kurtosis/skewness tests and for outlying variances using Cochran test.

Table 5 shows a summary of the statistical analysis for ERM-CA616, where *s* stands for standard deviation of the laboratories' means.

Table 5. Statistical evaluation of technically accepted datasets

	number of individual data	outlier means	normality	<i>s</i>	unit
ammonium ^a	60	-	yes	0.017	mg/L
calcium	72	L3	yes (99 %) ^b	2.2	mg/L
chloride	60	L5	yes (99 %) ^b	1.3	mg/L
magnesium	72	L3	yes	0.4	mg/L
<i>ortho</i> -phosphate	66	L10	yes	0.11	mg/L
potassium	66	-	yes	0.18	mg/L
sodium	72	L2	yes	1.3	mg/L
pH (20 °C)	72	-	yes	0.26	-
conductivity (20 °C)	72	L3	no	8	μS/cm

^adatasets obtained by photometric methods

^bconfidence level

For each parameter, there is at least one laboratory reporting an outlying mean result (with the exception of ammonium, potassium and pH). No technical reason was found for excluding these results and, considering the associated measurement uncertainty reported by the concerned laboratories, the measured values are not significantly different from the certified value. For these reasons the results were retained for the calculation of the mean and uncertainty of characterization (u_{char}).

Most datasets follow or are close to normal distributions, average and standard deviations are therefore meaningful estimators for the expected value and its variation. The results for conductivity are an exception. This is caused by the result of laboratory L3 which is classified as statistical outlier, but based on the result of the check described above, it was decided to keep the dataset in the calculation of the certified value.

In Table 6 the characterisation results of the groundwater material, expressed as the mean of means of the accepted datasets, are presented. The relative standard error of the mean of

means is used as an estimation of the uncertainty contribution of the characterisation exercise ($u_{\text{char,rel}}$).

Table 6. Characterisation results

	Mean of means	unit	p	$\text{RSD}_{\text{average}} [\%]$	$\text{RSE}_{\text{average}} [\%]$ $u_{\text{char,rel}}$
ammonium ^a	0.429	mg/L	10	3.9	1.2
calcium	42.6	mg/L	12	5.2	1.5
chloride	44.6	mg/L	10	2.8	0.9
magnesium	10.1	mg/L	12	4.1	1.2
<i>ortho</i> -phosphate	2.24	mg/L	11	4.8	1.5
potassium	5.79	mg/L	11	3.2	1.0
sodium	27.9	mg/L	12	4.8	1.4
pH (20 °C)	7.12	-	12	3.7	1.1
conductivity (20 °C)	426	μS/cm	12	1.9	0.5

^adatasets obtained by photometric methods

p = number of accepted datasets

10 Certified values and uncertainties

The certified values of groundwater ERM-CA616 were calculated as the unweighted mean of the means of the accepted datasets (see Table 6).

The relative combined uncertainty of the certified values of the CRM consists of uncertainties related to characterisation (u_{char}), between bottle heterogeneity (u_{bb}) and long-term storage (u_{Its}) [13].

- u_{char} was estimated as the standard deviation of the mean of laboratory means, i.e. s/\sqrt{p} with s and p taken from Table 5 and Table 6.
- u_{bb} was estimated as the larger value between the standard deviation between-units (s_{bb}) and the maximum heterogeneity potentially hidden by method repeatability (u_{bb}^*), or as u_{rect} in the case of ammonium, calcium, *ortho*-phosphate and potassium (see Table 1).
- u_{Its} was estimated from 1 year and 2 years long-term stability results combined at 18 °C (with the exception of pH for which only the 2 years data were considered) for a time frame of 2 years (see Table 3).

These uncertainties were combined quadratically to estimate the relative combined uncertainty of the certified value $u_{\text{CRM,rel}}$ according to:

$$\mathbf{u}_{\text{CRM,rel}} = \sqrt{\mathbf{u}_{\text{bb,rel}}^2 + \mathbf{u}_{\text{Its,rel}}^2 + \mathbf{u}_{\text{char,rel}}^2} \quad (8)$$

The relative expanded uncertainty $U_{\text{CRM,rel}}$ is given by the following expression, where $k = 2$ is chosen as coverage factor to provide a confidence level of approximately 95 %:

$$U_{\text{CRM,rel}} = k \cdot \mathbf{u}_{\text{CRM,rel}} \quad (9)$$

The absolute expanded uncertainty U_{CRM} is then calculated by rounding up the value obtained multiplying the certified value with the relative expanded uncertainty $U_{\text{CRM,rel}}$.

The various uncertainty contributions, the expanded uncertainties and the certified values are summarised in Table 7.

Table 7. Certified values and uncertainty budget for calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium, pH and conductivity in ERM-CA616

	$u_{\text{bb,rel}}$ [%]	$u_{\text{Its,rel}}$ [%]	$u_{\text{char,rel}}$ [%]	$U_{\text{CRM,rel}}$ ($k=2$) [%]	Certified value	U_{CRM} ($k=2$)	unit
calcium	0.2	0.4	1.5	3.2	42.6	1.4	mg/L
chloride	0.1	0.2	0.9	1.9	44.6	0.9	mg/L
magnesium	0.2	0.4	1.2	2.5	10.1	0.3	mg/L
<i>ortho</i> -phosphate	1.2	1.0	1.5	4.3	2.24	0.10	mg/L
potassium	0.7	0.4	1.0	2.4	5.79	0.15	mg/L
sodium	0.3	0.3	1.4	2.9	27.9	0.8	mg/L
pH (20 °C)	0.6	0.2	1.1	2.4	7.12	0.18	-
conductivity (20 °C)	0.1	0.1	0.5	1.1	426	5	μS/cm

Annex 4 summarises the results of the characterisation exercise and presents as well a graphical depiction of the assigned values, together with averages and standard deviations of the individual laboratories for calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium, pH and conductivity with the participating laboratories encrypted by codes (L0 to L12).

11 Additional material information

The certification of the mass concentration of ammonium in ERM-CA616 was judged impossible, due to the suspect of a possible method-dependant effect in the quantification: the two laboratories using IC delivered consistently higher results than all the other laboratories, all using spectrophotometric methods. It was consequently decided to assign two values for ammonium as additional material information, one based on the datasets obtained by spectrophotometry and the other one based on ion chromatography (as mean of two datasets) (see Table 8). Annex 5 summarises the data used in the calculation of these ammonium values.

Table 8. Ammonium values (expressed as mass concentration) for ERM-CA616

	p	[mg/L]
ammonium (as obtained by spectrophotometry)	10	0.429
ammonium (as obtained by IC-CD)	2	0.583

p = number of accepted datasets

12 Metrological traceability

Laboratories quantified the analytes using different and independent analytical methodologies, both regarding sample preparation as well as measurement principles, except for pH and conductivity. The calibrants employed were either commercially available, in-house gravimetrically prepared or CRMs, all traceable to the SI. For calcium, chloride, magnesium, *ortho*-phosphate, potassium and sodium, the agreement between the results confirms absence of any significant method bias and demonstrates the identity of the analytes. Only validated methods were used. Agreement with the certified values of the quality control materials further proved absence of significant bias, correctness of the calibration curves and proper calibration of all relevant input parameters.

The realisation of the above-mentioned conditions demonstrates that the certified values are traceable to the International System of Units (SI).

13 Commutability

ERM-CA616 is a natural groundwater. Moreover, the laboratories participating in the characterisation study have been selected such as to provide a large variety of analytical methods, regarding sample preparation, calibration and detection. The agreement between the

results obtained, leading to the certification of several parameters, shows that ERM-CA616 exhibits the same behaviour as a typical laboratory sample and confirms its commutability.

14 Instructions for use

14.1 Storage conditions

The material shall be stored at $+18\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ in the dark. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of open samples.

14.2 Minimum sample intake

The minimum amount of sample to be used is 0.005 mL for chloride, 0.1 mL for *ortho*-phosphate, 0.5 mL for calcium, magnesium and sodium, 2 mL for potassium and 10 mL for pH and conductivity.

14.3 Safety precautions

The usual laboratory safety measures apply.

14.4 Intended use

ERM-CA616 is intended for method validation and quality control purposes. Samples should be allowed to equilibrate to room temperature (20 -25 °C) before use.

14.5 Use of the certified value

For assessing the trueness of an analytical method, the CRM is analysed by the laboratory and the result is compared to the certified value as described in ERM Application Note 1 [12].

A result is unbiased if the combined uncertainty of measurement and certified value covers the difference between the certified value and the measurement result:

- Calculate the absolute difference between the mean of the CRM measurement results and the certified value (Δ_m).
- Convert the expanded uncertainty of the certified value U_{CRM} into a standard uncertainty (u_{CRM}) by dividing U_{CRM} with the coverage factor $k=2$.
- Combine the standard uncertainty of the measurement result (u_m) with the uncertainty of the certified value (u_{CRM}) as follows:

$$u_{\Delta} = \sqrt{u_m^2 + u_{CRM}^2} \quad (10)$$

If $\Delta_m < 2 \cdot u_{\Delta}$, there is no significant difference between the measurement result and the certified value, at a confidence level of about 95 %.

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Annex 1a

Homogeneity data for ammonium, calcium, chloride, magnesium, *ortho*-phosphate, potassium and sodium in ERM-CA616 expressed as mg/L

Ampoule number	Ammonium		Calcium		Chloride		Magnesium		<i>Ortho</i> -phosphate		Potassium		Sodium	
	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2	replic.1	replic.2
34	0.421	0.421	39.80	39.93	44.62	44.77	9.908	9.994	2.353	2.375	5.525	5.516	27.315	27.307
164	0.415	0.415	39.82	39.75	44.65	44.64	9.817	9.946	2.334	2.367	5.584	5.436	27.075	27.112
283	0.426	0.426	39.82	39.96	44.70	44.65	9.852	10.010	2.321	2.353	5.499	5.517	27.282	27.421
426	0.418	0.418	39.86	40.14	44.74	44.61	9.906	9.999	2.349	2.354	5.492	5.513	26.959	27.221
593	0.417	0.417	40.03	40.16	44.86	44.62	9.917	10.020	2.285	2.356	5.579	5.521	27.271	27.282
716	0.422	0.422	39.85	39.96	44.68	44.80	9.900	9.994	2.319	2.334	5.554	5.484	27.035	27.100
867	0.416	0.416	39.89	39.91	44.68	44.66	9.972	9.987	2.280	2.306	5.585	5.490	27.172	26.987
985	0.412	0.414	39.82	39.99	44.85	44.65	9.860	10.000	2.260	2.309	5.593	5.562	27.090	27.293
1142	0.404	0.404	40.12	40.08	44.75	44.66	9.976	10.030	2.299	2.324	5.546	5.548	27.294	27.165
1277	0.408	0.408	39.85	40.20	44.71	44.61	9.920	9.994	2.247	2.287	5.590	5.606	27.275	27.265
1411	0.411	0.411	40.03	40.20	44.68	44.73	9.928	10.030	2.314	2.351	5.528	5.542	27.121	27.203
1565	0.407	0.407	39.92	39.92	44.61	44.70	9.840	9.941	2.256	2.300	5.525	5.538	27.252	27.163

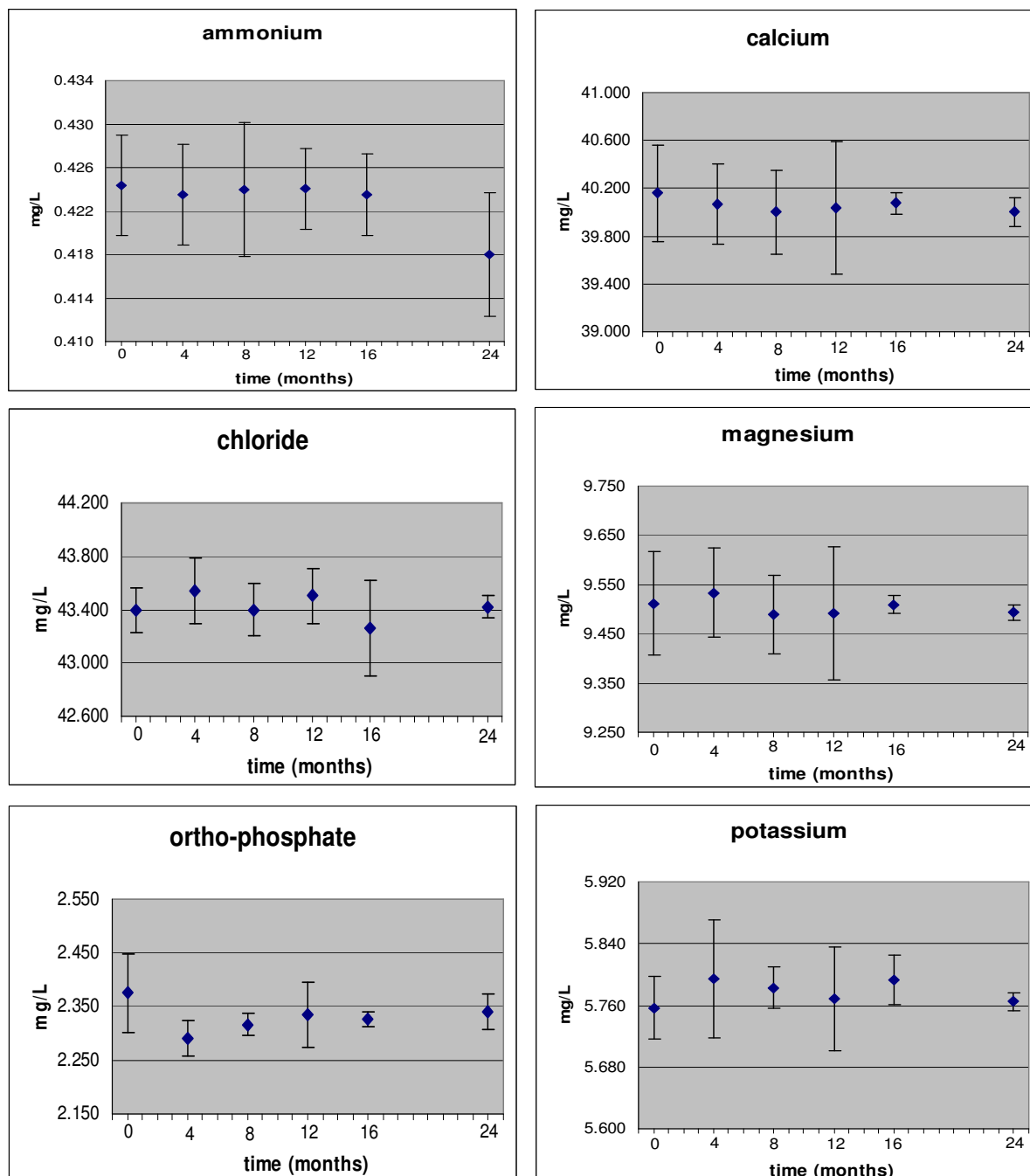
Annex 1b

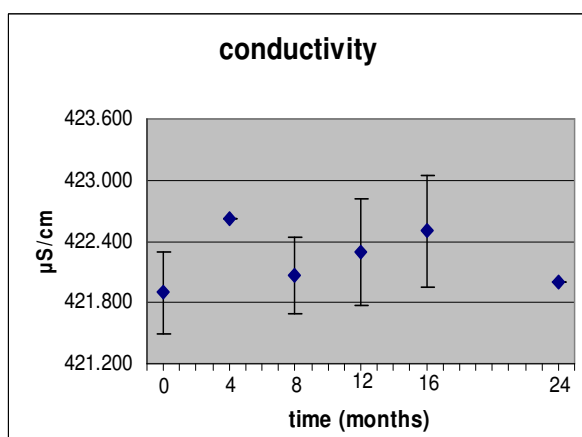
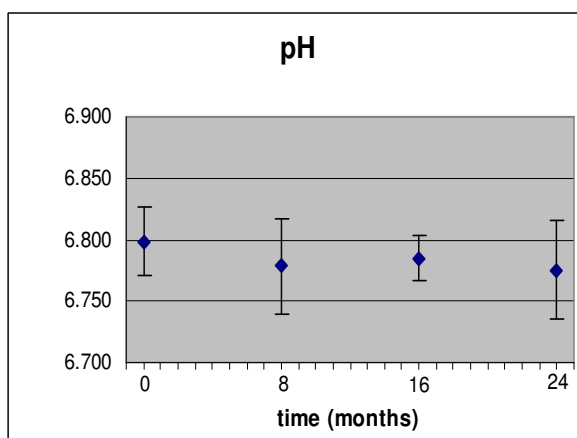
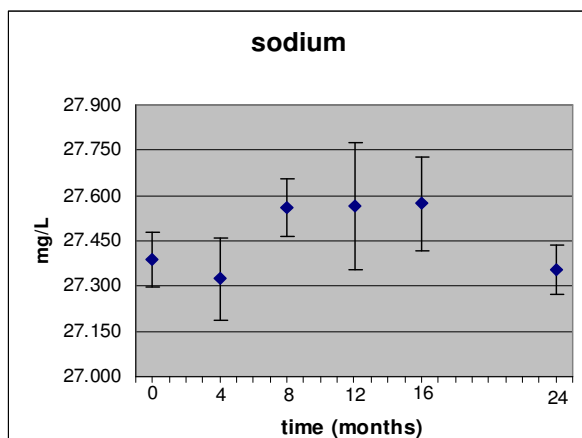
Homogeneity data for pH and conductivity in ERM-CA616

Ampoule number	pH		Conductivity [μS/cm]	
	replic.1	replic.2	replic.1	replic.2
89	6.89	6.93	426	426
218	6.84	6.95	426	426
377	6.84	6.94	426	426
510	6.83	6.92	427	427
663	6.88	6.93	426	425
774	6.87	6.98	425	426
913	6.89	6.97	426	425
1082	6.88	6.95	425	425
1201	6.81	6.91	425	426
1347	6.90	7.00	426	427
1488	6.86	6.90	426	426
1619	6.96	7.02	425	425

Annex 2: Graphical depictions of long-term stability data for ammonium, calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium, pH and conductivity in ERM-CA616

The graphs report ampoule averages per time point and their 95 % confidence intervals based on the standard deviations of the replicates per time (12 for points 0 and 8 months, 6 for points 4, 12, 16 and 24 months). The uncertainty bars of the pH measurements represent the 95 % confidence intervals based on the standard deviations of 6 replicates per time point.





Annex 3. Detailed description of the analytical techniques used in the characterization of ERM-CA616

Ammonium

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	none	5	PHOT, CFA Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0.01, 0.03, 0.05, 0.08, 0.1, 0.2, 0.5, 0.8, 1.0 NH ₄ Cl	0.009
L1	none	~25	PHOT, 660 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0, 0.1, 0.6, 1.2, 2 [N] Commercially available mixed standard	0.05[N]
L2	Dilution (when necessary)	2	IC CD 25 µL injection volume, pre-column Dionex CG15, column Dionex CS15, eluent: H ₂ SO ₄ /CH ₃ CN, CSRS ultra suppressor	External calibration 0.5, 1, 5, 10, 15, 20 NH ₄ Cl	0.2
L3	none	5	PHOT, 690 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0.1, 0.2, 0.5 NH ₄ Cl	0.1
L4	dilution	5	IC CD 100 µL injection volume, pre-column Dionex CG12A, column Dionex CS12A, eluent: 20 mM methane sulfonic acid, CAES electrolytic suppressor	Quadratic 0.064, 0.13, 0.26, 0.51, 1.29, 2.58 NH ₄ Cl >99.99	0.09
L5	none	0.1	PHOT, 660 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Polynomial (2 nd order) 0, 0.05, 0.1, 0.3, 0.6, 1.2, 2.0 Commercially available standard	0.02
L6	dilution	2	PHOT, SFA, 660 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0.070, 0.100, 0.150, 0.200, 0.300, 0.350 (NH ₄) ₂ SO ₄ in water	0.070

Ammonium (continued)

L8	none	~1.5	PHOT Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0.064, 0.129, 0.514, 1.029, 1.286 In-house prepared NH ₄ calibrant	0.08
L9	-	10	PHOT Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear, 8 points 0+ 0.01-0.8 [N] NH ₄ Cl	0.01[N]
L10	dilution	0.23	PHOT, SFA Modified Berthelot reaction	Linear 0.1, 0.2, 0.3, 0.4, 0.5 NH ₄ Cl solid p.a.	0.1
L11	none	0.120	PHOT, 660 nm Reaction with dichloroisocyanurate and salicylate (indophenol method)	Linear 0, 0.4, 0.8, 1.2, 1.6, 2 [N] NH ₄ Cl	0.16 [N]
L12	Dilution 1:2.5	10	PHOT, batch photometry Reaction with salicylate and dichloroisocyanurate (indophenol method)	Linear 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 Commercially available standard, Certipur1000 mg/L	0.0182

Calcium

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	Acidification with HNO ₃	4.95	ICP-OES	Linear 1, 10, 50, 100 Ca(NO ₃) ₂	0.14
L1	Acidification with HNO ₃	~25	ICP-OES	Linear, weighted fit, weighing=1/signal int. 0.1, 0.5, 2, 5, 20, 50 Commercially available calcium standard	0.01
L2	Dilution	0.5	ICP-OES	Linear, 4 points incl. blank 2, 4, 10 Ca(NO ₃) ₂	0.4
L3	Acidification to pH 2 and dilution (if necessary)	5	F-AAS	Linear 1.0, 2.5, 5.0, 7.5 Commercially available calcium standard	0.1
L4	dilution	5	IC CD 100 µL injection volume, pre-column Dionex CG12A, column Dionex CS12A, eluent: 20 mM methane sulfonic acid, CAES electrolytic suppressor	Linear 0.125, 0.25, 0.5, 1.5, 5, 10, 25 CaCO ₃ solution	0.13
L5	Acidification with HNO ₃	-	ICP-OES	Polynomial (2 nd order) 0, 5, 10, 20, 50, 100, 200 Commercially available calcium standard	0.005
L6	dilution with 1 % HNO ₃	5	ICP-OES	Linear 5, 10, 15, 20, 30, 40 CaCO ₃ in 5 % HNO ₃	5
L8	dilution	~2.5	ICP-MS	Y=aX+blank 0, 6, 12, 30 Commercially available calcium standard	0.1

Calcium (continued)

L9	none	2	ICP-OES	Linear 0, 50, 150 Commercially available calcium standard	0.01
L10	none	10	ICP-OES	2-points calibr. 0, 50 CaCO ₃	1
L11	none	3	ICP-OES	Linear 2, 10, 50 Commercially available multielement standard	0.046
L12	Acidification with 2 % HNO ₃	5	ICP-OES	2 nd order 1.0, 5.0, 10, 20, 50, 100, 150, 200 Commercially available calcium standard 10 g/L	0.0586

Chloride

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	dilution	1	IC CD 25 µL injection volume, pre-column IonPac AG12, column IonPac AS12, eluent: 2.7 mM Na ₂ CO ₃ +0.3 mM NaHCO ₃ , AMMS 300 suppressor	Quadratic 0.5, 1, 2, 4, 8, 12, 15 NaCl	0.32
L1	none	~25	PHOT, 480 nm Automated Ferricyanide Method	2 nd order 0, 25, 150, 300, 500 Commercially available mixed standard	0.01
L2	dilution	0.2	IC CD pre-column Dionex AG4, column Dionex AS4, eluent: carbonate/bicarbonate	External calibration 0.2, 0.5, 1, 3, 5 NaCl	0.2
L4	dilution	5	IC CD 100 µL injection volume, pre-column Dionex AG19, column Dionex AS19, eluent: 19 mM KOH, ASRS electrolytic suppressor	Linear 0.05, 0.1, 0.2, 0.5, 2, 5, 10 NaCl >99.99	0.06
L5	none	0.005	IC CD 5 µL injection volume, pre-column IonPac AG19, column IonPac AS19, EluGen Cartridge Potassium Hydroxide, ASRS ultra suppressor	Linear 5, 10, 25, 50, 125, 250 Commercially available standard	0.02
L6	dilution	10	IC CD 50 µL injection volume, pre-column Dionex AG14A, column Dionex AS14A, eluent: 8 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , ASRS 300 Dionex suppressor	Linear 7.5, 20, 30 KCl in water	7.5

Chloride (continued)

L8	none	~1	IC CD 50 µL injection volume, pre-column IonPac AG4a, column IonPac AS4a-SC, eluent: 1.8 mM Na ₂ CO ₃ +1.7 mM NaHCO ₃ , electrochemical suppression	Point-to-point 1, 4, 6, 10, 20, 30, 60 In-house prepared calibrant	0.05
L9	dilution	3	IC CD guard column IonPac AG14A, column AS14A, eluent: 3.5 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , ASRS Ultra II suppressor	Quadratic 1.0, 2.5, 5.0, 10 NaCl	3
L10	dilution	0.050	IC CD 50 µL loop, RP-guard Metrohm, Metrosepp A supp 7 Metrohm, ASRS suppressor	Quadratic 1, 2, 4, 6, 8, 10 NaCl	1
L12	none	0.1	IC CD 100 µL injection volume, guard column AG14, column AS14, eluent: 3.5 mM Na ₂ CO ₃ +1 mM NaHCO ₃ , autorecycle mode suppression	Cubic equation 1.0, 2.0, 5.0, 10.0, 25, 50, 100, 150, 200 Commercially available standard Certipur 1000 mg/L	0.401

Magnesium

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	Acidification with HNO ₃	4.95	ICP-OES	Linear 1, 10, 50, 100 Mg(NO ₃) ₂	0.18
L1	Acidification with HNO ₃	~25	ICP-OES	Linear, weighted fit, weighing=1/signal int. 0.1, 0.5, 2, 5, 20, 50 Commercially available magnesium standard	0.01
L2	Dilution	0.5	ICP-OES	Linear, 4 points incl. blank 2, 4, 8 Mg(NO ₃) ₂	0.2
L3	Acidification to pH 2 and dilution (if necessary)	5	F-AAS	Linear 0.1, 0.2, 0.5, 0.75, 1.0, 1, 5, 10 Commercially available magnesium standard	0.1
L4	dilution	5	IC CD 100 µL injection volume, pre-column Dionex CG12A, column Dionex CS12A, eluent: 20 mM methane sulfonic acid, CAES electrolytic suppressor	Linear 0.025, 0.05, 0.1, 0.3, 1, 2, 5 Mg(NO ₃) ₂ solution	0.03
L5	Acidification with HNO ₃	-	ICP-OES	Polynomial (2 nd order) 0, 5, 10, 20, 50, 100, 200 Commercially available magnesium standard	0.02
L6	dilution with 1 % HNO ₃	5	ICP-OES	Linear 1, 2, 3, 4, 6, 8 Mg in 5 % HNO ₃	1

Magnesium (continued)

L8	none	~2.5	ICP-MS	Y=aX+blank 0, 2, 4, 10 Commercially available magnesium standard	0.005
L9	none	2	ICP-OES	Linear 0, 5, 30 Commercially available magnesium standard	0.01
L10	none	10	ICP-OES	Two-points calibr. 0, 50 Mg(NO ₃) ₂ ·6H ₂ O	1
L11	none	3	ICP-OES	Linear 0.2, 1, 5* Commercially available multielement standard	0.064
L12	Acidification with 2 % HNO ₃	5	ICP-OES	2 nd order 0.5, 1.0, 2.5, 5.0, 12.5, 25, 50 Commercially available magnesium standard 1000 mg/L	0.0631

*even though the highest calibration point was below the measurement result, L11 ensured the correct quantification of the peak through their method validation study, in which linearity is proven until 250 mg/L.

Ortho-phosphate

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	dilution	2	PHOT Ammonium molybdate method	Linear 0.01, 0.03, 0.06, 0.12, 0.18, 0.24, 0.30, 0.36, 0.42 KH ₂ PO ₄	0.002
L1	none	~25	PHOT, 880 nm Ammonium molybdate method	Linear 0, 12.5, 75, 150, 250 [P] Commercially available single element standard	0.01[P]
L2	dilution	5	PHOT Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	External calibration 0.00, 0.184, 0.307, 0.614, 1.228, 1.842, 2.456, 3.070 P ⁵⁺ in water (stabilised)	0.06
L4	dilution	~11	PHOT, 890 nm Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	Linear 0.012, 0.025, 0.04, 0.05, 0.09, 0.18, 0.31, 0.61, 1.23 KH ₂ PO ₄ 99,999 %	0.015
L5	none	0.1	PHOT, 880 nm Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	Linear 0, 0.1, 0.2, 0.5, 1, 1.5, 2, 2.57 Phosphate standard solution	0.04
L6	dilution	10	IC CD 50 µL injection volume, column Dionex AS14A with a pre-column Dionex AG14A, eluent: 8mM Na ₂ CO ₃ +1mM NaH CO ₃ , ASRS 300 Dionex suppressor	Linear 0.375, 0.600, 0.900, 1.125, 1.500, 2.250 (P ₂ O ₅) KH ₂ PO ₄ in water	0.375(P ₂ O ₅)
L8	dilution	~1.5	PHOT Ammonium molybdate method	Linear 0.077, 0.153, 0.613, 1.226, 1.532 In-house prepared PO ₄ calibrant	0.06

Ortho-phosphate (continued)

L9	-	10	PHOT Ammonium molybdate method	Linear, 8 points 0+ 0.02-1.0 [P] KH ₂ PO ₄	0.005[P]
L10	dilution	0.6	PHOT, SFA, 880 nm Reaction with ammonium molybdate and potassium antimonyl tartrate, reduction with ascorbic acid	Linear 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 [P] KH ₂ PO ₄	0.05[P]
L11	none	0.072	PHOT, 880 nm Ammonium molybdate method	Linear 0.6, 1.2, 1.8, 2.4, 3 KH ₂ PO ₄	0.01
L12	Dilution 1:5	5	PHOT, batch photometry Ammonium molybdate method	Linear 0, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 Commercially available standard, Certipur1000 mg/L	0.0858

Potassium

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	Acidification with HNO ₃	4.95	ICP-OES	Linear 1, 10, 50, 100 KNO ₃	0.14
L1	Acidification with HNO ₃	~25	ICP-OES	Linear, weighted fit, weighing=1/signal int. 0.1, 0.4, 1, 4, 10 Commercially available potassium standard	0.005
L3	Acidification to pH 2 and dilution (if necessary)	5	F-AAS	Linear 0.2, 0.5, 1.0, 1.5 Commercially available potassium standard	0.1
L4	dilution	5	IC CD 100 µL injection volume, pre-column Dionex CG12A, column Dionex CS12A, eluent: 20 mM methane sulfonic acid, CAES electrolytic suppressor	Linear 0.025, 0.05, 0.1, 0.3, 1, 2, 5 KNO ₃ solution	0.07
L5	Acidification with HNO ₃	-	ICP-OES	Polynomial (2 nd order) 0, 5, 10, 20, 50, 100, 200 Commercially available potassium standard	0.015
L6	dilution with 1 % HNO ₃	5	ICP-OES	Linear 1, 2, 3, 4, 6, 8 KNO ₃ in 5 % HNO ₃	1
L8	none	~2.5	ICP-MS	Y=aX+blank 0, 2, 4, 10 Commercially available potassium standard	2
L9	dilution	2	ICP-OES	Linear 0, 1, 5 Commercially available potassium standard	0.05

Potassium (continued)

L10	none	10	ICP-OES	Two-points calibr. 0, 50 KNO ₃	1
L11	none	2.5	ICP-OES	Linear 0.2, 2.5, 20 Commercially available multielement standard	0.367
L12	Acidification with 2 % HNO ₃	5	ICP-OES	2 nd order 0.4, 1.0, 2.0, 5.0, 10, 20 Commercially available potassium standard 400 mg/L	0.0255

Sodium

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: type, points (mg/L), calibrant</i>	<i>LOQ (mg/L)</i>
L0	Acidification with HNO ₃	4.95	ICP-OES	Linear 1, 10, 50, 100 NaNO ₃	0.11
L1	Acidification with HNO ₃	~25	ICP-OES	Linear, weighted fit, weighing=1/signal int. 0.1, 0.5, 2, 5, 20, 50 Commercially available sodium standard	0.01
L2	Dilution	0.5	ICP-OES	Linear, 4 points incl. blank 2, 4, 10 NaNO ₃	1
L3	Acidification to pH 2 and dilution (if necessary)	5	F-AAS	Linear 0.2, 0.5, 1.0, 2.0, 10, 50, 100 commercially available sodium standard	0.2
L4	dilution	5	IC CD 100 µL injection volume, pre-column Dionex CG12A, column Dionex CS12A, eluent: 20 mM methane sulfonic acid, CAES electrolytic suppressor	Linear 0.025, 0.05, 0.1, 0.3, 1, 2, 5 NaNO ₃ solution	0.03
L5	Acidification with HNO ₃	-	ICP-OES	Polynomial (2 nd order) 0, 5, 10, 20, 50, 100, 200 Commercially available sodium standard	0.03
L6	dilution with 1 % HNO ₃	5	ICP-OES	Linear 1, 2, 3, 4, 6, 8 NaNO ₃ in 5 % HNO ₃	5
L8	none	~2.5	ICP-MS	Y=aX+blank 0, 6, 12, 30 Commercially available sodium standard	0.3

Sodium (continued)

L9	none	2	ICP-OES	Linear 0, 5, 50 Commercially available sodium standard	0.01
L10	dilution	10	ICP-OES	Two-points calibr. 0, 25 Na ₂ CO ₃	1
L11	none	2.5	ICP-OES	Linear 0.2, 2.5, 20* Commercially available multielement standard	0.182
L12	Acidification with 2 % HNO ₃	5	ICP-OES	2 nd order 0.5, 1.0, 2.0, 5.0, 10, 25, 50, 100 Commercially available sodium standard 2000 mg/L	0.0172

*even though the highest calibration point was below the measurement result, L11 ensured the correct quantification of the peak through their method validation study, in which linearity is proven until 500 mg/L.

pH (at 20 °C)

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: calibrant, points</i>
L0	none	-	potentiometry measurements carried out at 20 °C	Commercially available standards Buffers at pH 4.01 and 7.00
L1	none	~40	potentiometry	Commercially available standards Buffers at pH 2.00, 4.01, 7.00, 10.00
L2	none	15	potentiometry	Commercially available standards Buffers at pH 2.00, 9.21
L3	none	20	potentiometry measurements carried out at 20 °C	Commercially available standards Buffers at pH 4.0, 7.0, 10.0
L5	none	15	potentiometry	Commercially available standards Buffers at pH 4.00 and 7.00
L6	none	-	potentiometry	Commercially available standards Buffers at pH 4.00, 7.00 and 9.00
L7	none	~30	Potentiometry measurements carried out at 20 °C	Commercially available standards Buffers at pH 6.88 and 9.23
L8	none	~10	potentiometry	Commercially available standards Buffers at pH 4.00 and 7.00
L9	none	10	Potentiometry measurements carried out at 20 °C	Commercially available stock solution Buffers at pH 7.00 and 10.00
L10	none	20	potentiometry measurements carried out at 20 °C	Commercially available standards Buffers at pH 7.02 and 10.13
L11	none	50	potentiometry	Commercially available standards Buffers at pH 4.0, 7.0, 10.0
L12	none	25	potentiometry	Commercially available standards Certipur Buffers at pH 6.88 and 9.22

Conductivity (at 20 °C)

<i>Lab</i>	<i>Sample pre-treatment</i>	<i>Sample intake (mL)</i>	<i>Analytical method and determination</i>	<i>Calibration: calibrant, points</i>
L0	none	not stated	conductimetry measurements carried out @ 20 °C	KCl 0.01 M
L1	none	~40	conductimetry	KCl 0.1 M
L2	none	15	conductimetry	KCl 3 and 10 M
L3	none	20	conductimetry	KCl (1413 µS) 14.13 µS, 1413 µS
L5	none	15	conductimetry	Commercially available standard 1276 µS/cm
L6	none	not stated	conductimetry	KCl 0.001, 0.002 and 0.01 M
L7	none	~30	conductimetry measurements carried out @ 20 °C	Commercially available KCl solutions 1273 µS/cm
L8	none	~10	conductimetry	KCl solution 0.01 M
L9	none	10	conductimetry	Commercially available solution 1413 µS/cm
L10	none	20	conductimetry measurements carried out @ 20 °C	NaCl 0.05 m/m %
L11	none	50	conductimetry	Commercially available standard NaCl
L12	none	20	conductimetry	Commercially available standards Certipur 0.147 mS (T=25 °C), 0.133 mS (T=20 °C)

Annex 4. Characterisation measurement results used in the certification of calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium, pH and conductivity in ERM-CA616

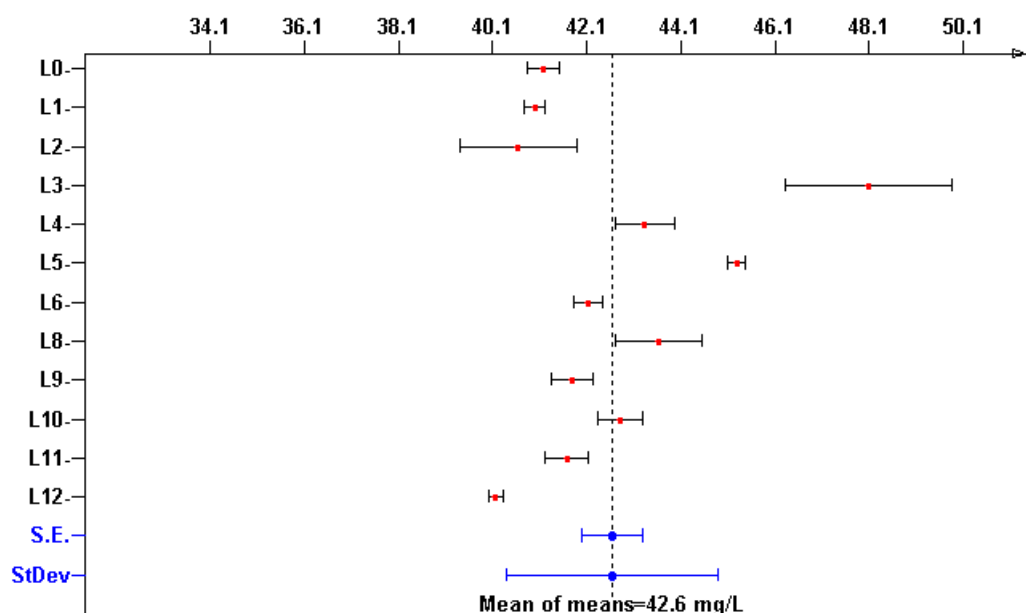
The tables in this annex contain also the datasets that were discarded for technical reasons. These data are presented in *italics* and are given for informative purposes only. They are not reported in the graphs.

The bars in the graphs represent *s*, standard deviation of the measurement results. The X axis range covers approximately ± 20 % of the mean.

Calcium

lab code	Replicates [mg/L]						mean	<i>s</i>
L0	41.11	40.81	40.97	41.27	41.78	41.1	41.173	0.335
L1	40.95	41.33	41.13	40.98	40.65	40.94	40.997	0.226
L2	41	39.5	40.1	41.8	42.3	39.2	40.650	1.257
L3	47.7	47.1	48.2	45.6	50.8	49.1	48.083	1.772
L4	43.53	42.08	43.67	43.62	43.58	43.55	43.338	0.618
L5	45.2	45	45.2	45.4	45.5	45.4	45.283	0.183
L6	42.1	42.3	42.0	42.2	42.5	41.6	42.117	0.306
L8	43	43	42.9	45.3	43.6	44	43.633	0.922
L9	41.48	42.02	41.14	41.88	42.38	41.86	41.793	0.432
L10	43.325	43.184	43.125	42.264	42.651	0.44	42.800	0.478
L11	41.73	41.42	41.36	41.28	41.69	42.57	41.675	0.474
L12	40.12	40.13	39.96	40.33	40.35	40.06	40.158	0.153

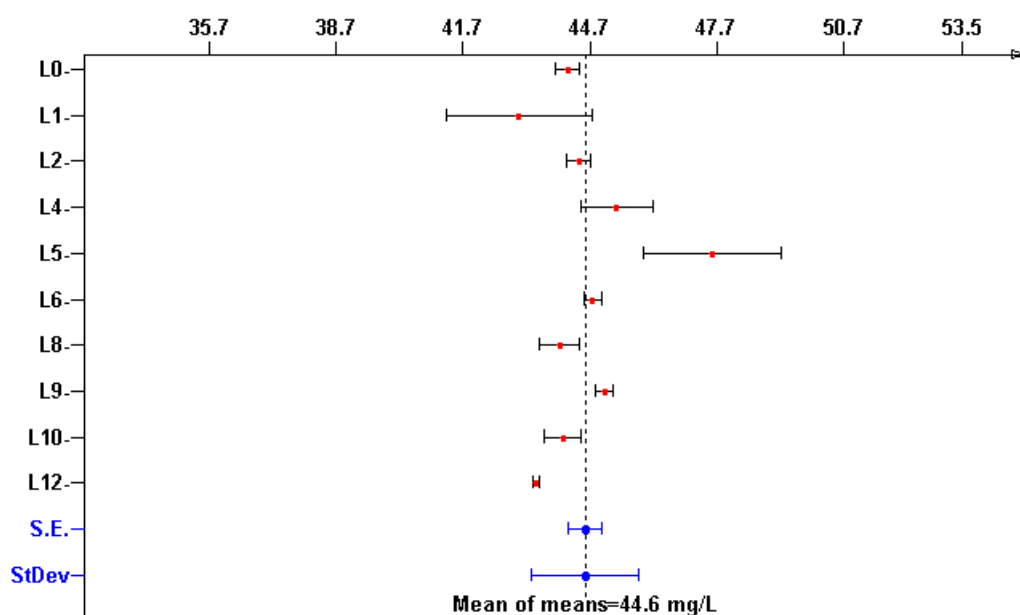
Laboratory means and their standard deviations



Chloride

lab code	Replicates [mg/L]						mean	s
L0	43.83	44.45	44.08	43.9	44.16	44.58	44.167	0.298
L1	40.846	42.283	41.665	44.828	43.503	45.016	43.024	1.708
L2	44.6	44.1	44.8	44.2	44.6	44.3	44.433	0.273
L3	41.1	40.9	41.5	40.7	41.5	40.6	41.050	0.389
L4	43.58	45.72	45.71	45.75	45.61	45.61	45.330	0.859
L5	45.1	49.1	49.5	46.8	47	48.1	47.600	1.635
L6	44.9	45	44.9	44.7	44.6	44.5	44.767	0.197
L8	43.63	44.05	44.13	44.61	43.24	44.24	43.983	0.482
L9	44.9	45	44.8	45.4	45.1	45.1	45.050	0.207
L10	43.9	44	44.9	44	44	43.6	44.067	0.437
L11	39.80	39.50	39.58	40.59	40.35	40.33	40.025	0.457
L12	43.4	43.43	43.55	43.38	43.3	43.46	43.420	0.084

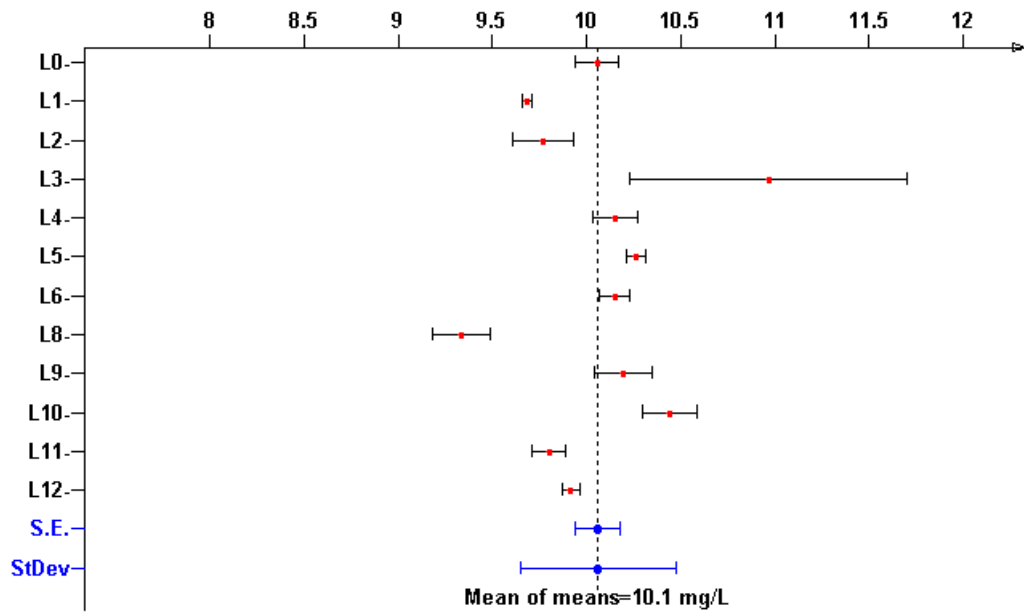
Laboratory means and their standard deviations



Magnesium

lab code	Replicates [mg/L]						mean	s
L0	10.01	9.95	9.92	10.12	10.2	10.13	10.055	0.111
L1	9.679	9.685	9.722	9.685	9.642	9.688	9.684	0.025
L2	9.91	9.65	9.66	9.91	9.93	9.56	9.770	0.165
L3	11.0	11.5	10.2	12.0	10.1	11.0	10.967	0.734
L4	10.18	9.91	10.22	10.19	10.2	10.2	10.150	0.118
L5	10.2	10.2	10.3	10.3	10.3	10.3	10.267	0.052
L6	10.1	10.1	10.1	10.1	10.3	10.2	10.150	0.084
L8	9.532	9.346	9.412	9.23	9.399	9.094	9.336	0.154
L9	9.975	10.11	10.14	10.2	10.37	10.37	10.194	0.155
L10	10.61	10.532	10.532	10.241	10.413	10.315	10.441	0.143
L11	9.79	9.76	9.78	9.69	9.81	9.97	9.800	0.093
L12	9.952	9.872	9.885	9.89	9.999	9.904	9.917	0.049

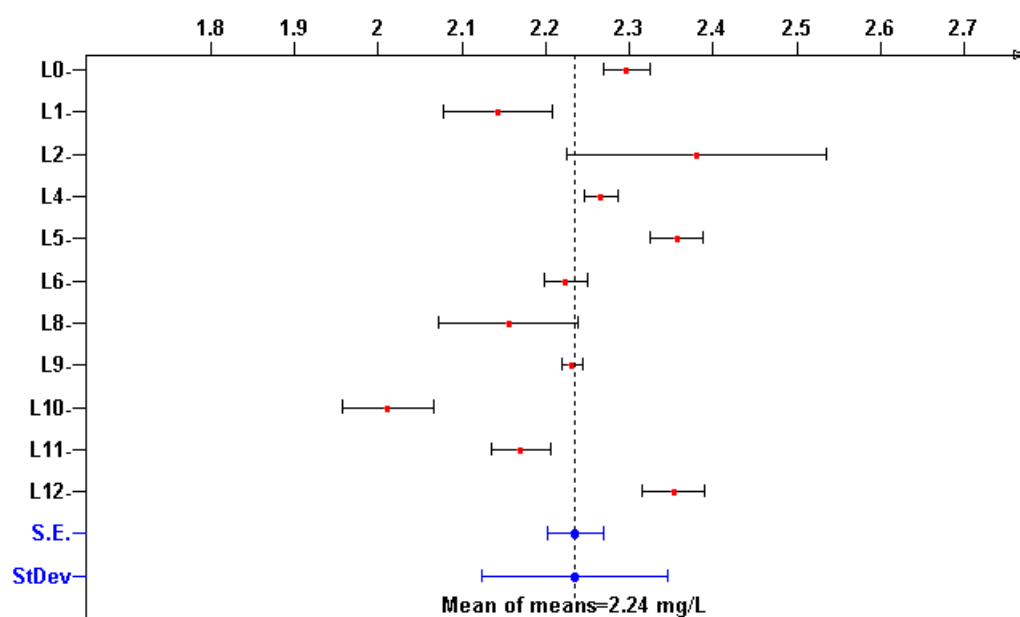
Laboratory means and their standard deviations



Ortho-phosphate

lab code	Replicates [mg/L]						mean	s
L0	2.27	2.33	2.28	2.3	2.27	2.33	2.297	0.028
L1	2.228	2.2	2.167	2.096	2.09	2.072	2.142	0.065
L2	2.68	2.3	2.25	2.36	2.3	2.39	2.380	0.155
L3	2.5	2.3	2.4	2.2	2.4	2.3	2.350	0.105
L4	2.286	2.287	2.274	2.252	2.263	2.235	2.266	0.020
L5	2.32	2.35	2.32	2.37	2.39	2.39	2.357	0.032
L6	2.23	2.23	2.22	2.22	2.26	2.18	2.223	0.026
L8	2.164	2.121	2.268	2.093	2.234	2.053	2.156	0.083
L9	2.235	2.235	2.229	2.251	2.217	2.223	2.232	0.012
L10	1.919	2.054	2.03	1.999	1.993	2.073	2.011	0.055
L11	2.13	2.18	2.14	2.2	2.15	2.22	2.170	0.036
L12	2.385	2.341	2.376	2.385	2.342	2.288	2.353	0.038

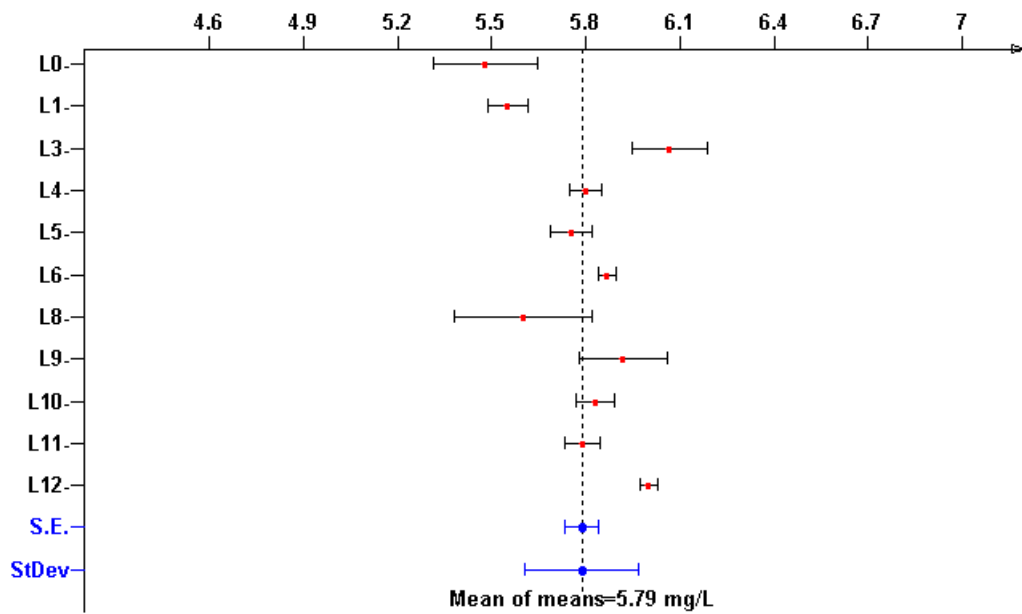
Laboratory means and their standard deviations



Potassium

lab code	Replicates [mg/L]						mean	s
L0	5.41	5.27	5.34	5.54	5.7	5.62	5.480	0.167
L1	5.579	5.626	5.605	5.527	5.522	5.448	5.551	0.065
L2	5.19	4.87	4.99	4.94	5.03	4.89	4.985	0.117
L3	6.0	6.1	6.0	6.0	6.3	6.0	6.067	0.121
L4	5.85	5.82	5.85	5.8	5.74	5.74	5.800	0.050
L5	5.79	5.79	5.78	5.63	5.72	5.8	5.752	0.066
L6	5.86	5.92	5.83	5.86	5.88	5.86	5.868	0.030
L8	5.7	5.5	6	5.4	5.5	5.5	5.600	0.219
L9	6.051	5.91	6.088	5.739	5.785	5.945	5.920	0.139
L10	5.919	5.815	5.899	5.795	5.799	5.764	5.832	0.062
L11	5.74	5.73	5.78	5.77	5.87	5.84	5.788	0.056
L12	6.00	6.00	6.00	5.97	6.05	5.98	6.000	0.028

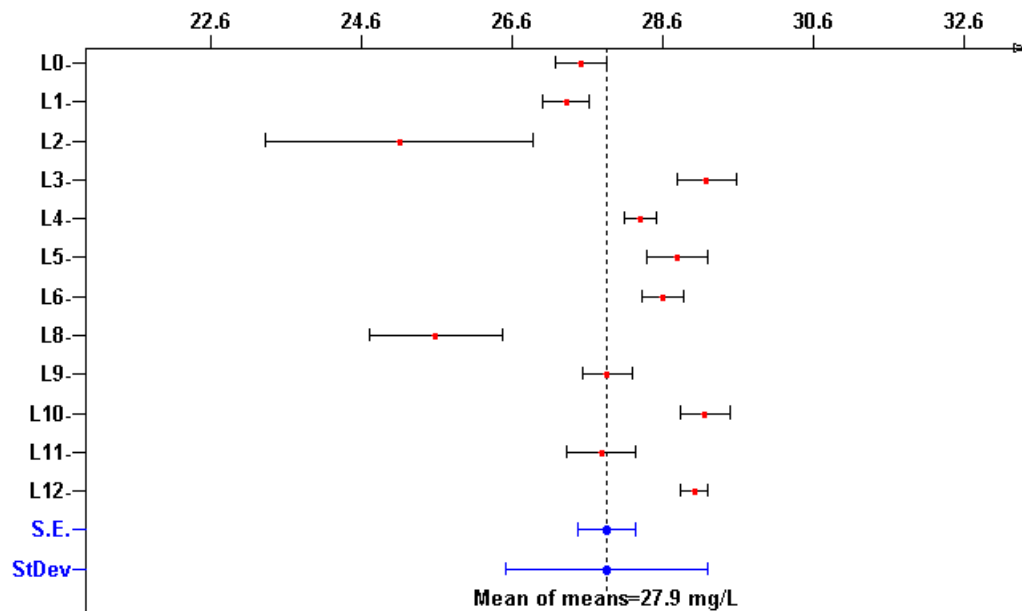
Laboratory means and their standard deviations



Sodium

lab code	Replicates [mg/L]						mean	s
L0	27.34	27.26	27.13	27.58	28.05	27.72	27.513	0.340
L1	27.56	27.38	27.39	27.3	26.72	27.53	27.313	0.307
L2	26.9	23	26.5	23.6	26.7	23.9	25.100	1.781
L3	28.9	28.9	29.6	28.7	29.5	29.5	29.183	0.392
L4	28.12	27.99	28.28	28.47	28.48	28.46	28.300	0.208
L5	28.9	29.0	28.8	29.1	28.0	29.0	28.800	0.405
L6	28.4	28.6	28.7	29.0	28.7	28.2	28.600	0.276
L8	25.84	24.69	24.62	25.33	26.93	26.1	25.585	0.887
L9	27.77	28.04	27.37	27.62	28.2	28.16	27.860	0.330
L10	28.776	28.857	29.035	29.196	29.532	29.558	29.159	0.333
L11	27.37	27.44	27.44	27.78	28.26	28.39	27.780	0.448
L12	28.83	28.83	29.10	29.21	29.20	28.93	29.017	0.176

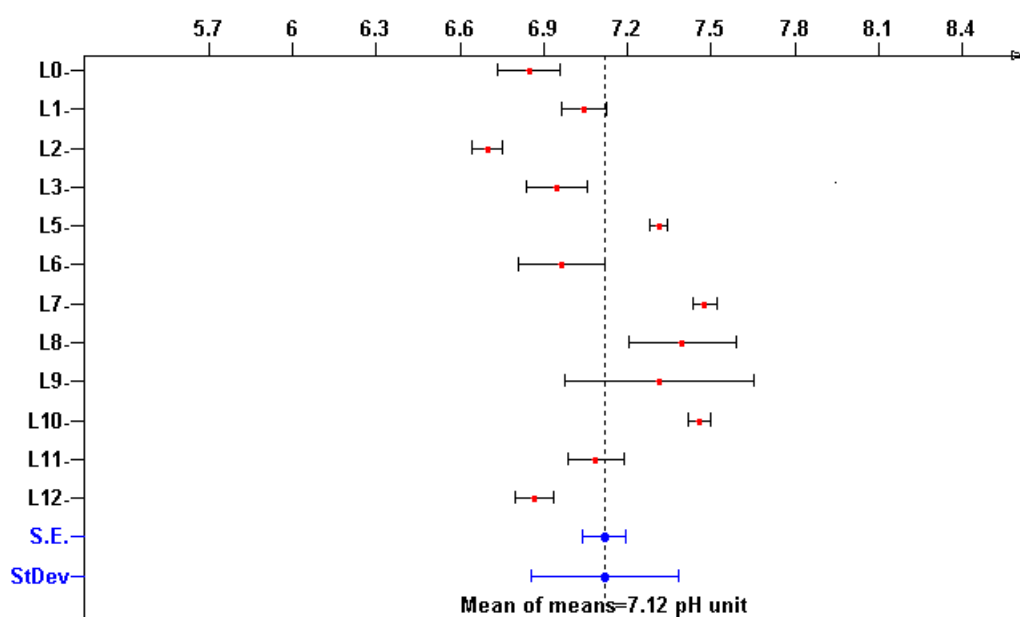
Laboratory means and their standard deviations



pH

lab code	Replicates (pH unit)						mean	s
L0	6.762	6.782	6.836	7.063	6.793	6.847	6.847	0.111
L1	6.96	7.01	6.95	7.12	7.1	7.13	7.045	0.082
L2	6.65	6.65	6.65	6.73	6.75	6.76	6.698	0.054
L3	6.85	6.83	7.05	6.86	7.04	7.05	6.947	0.110
L4	6.83	7.13	6.77	6.98	6.90	7.09	6.95	0.140
L5	7.27	7.3	7.31	7.35	7.3	7.34	7.312	0.029
L6	6.81	6.85	6.87	7.17	6.93	7.15	6.963	0.157
L7	7.439	7.494	7.498	7.542	7.44	7.447	7.477	0.042
L8	7.15	7.16	7.45	7.48	7.54	7.59	7.395	0.192
L9	7.05	7.02	7.8	6.99	7.5	7.52	7.313	0.339
L10	7.45	7.45	7.39	7.51	7.49	7.46	7.458	0.041
L11	6.99	7.03	6.99	7.1	7.2	7.21	7.087	0.100
L12	6.83	6.99	6.79	6.83	6.88	6.88	6.867	0.069

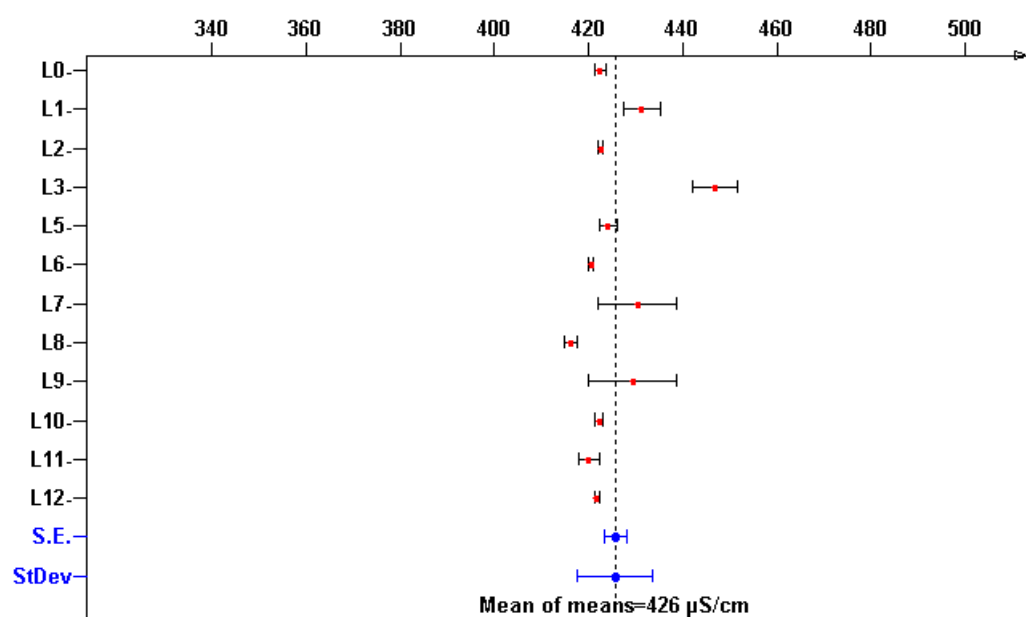
Laboratory means and their standard deviations



Conductivity

lab code	Replicates [$\mu\text{S/cm}$]						mean	s
L0	422	422	421	422	424	424	422.500	1.225
L1	439	430	429	430	432	428	431.333	3.983
L2	422	422	423	423	423	423	422.667	0.516
L3	445	440	450	443	452	451	446.833	4.875
L4	415.9	414.9	413.3	414.6	415.7	416.2	415.1	1.035
L5	423	427	426	422	424	423	424.167	1.941
L6	420	421	420	421	420	421	420.500	0.548
L7	434	446	427	425	426	425	430.500	8.313
L8	417.3	417.1	417.7	416.8	414.2	415.1	416.367	1.391
L9	420.332	422.136	437.47	421.234	433.862	441.078	429.352	9.199
L10	422	423	423	423	421	422	422.333	0.816
L11	418.5	418.5	418.5	419.6	423.2	422.3	420.100	2.116
L12	421	422	422	422	422	422	421.833	0.408

Laboratory means and their standard deviations



Annex 5. Characterization measurements used in the assignment of ammonium values as additional material information in ERM-CA616

The table contain also the datasets obtained by IC. These data are presented in *italics* and are given for informative purposes only. They are not reported in the graphs.

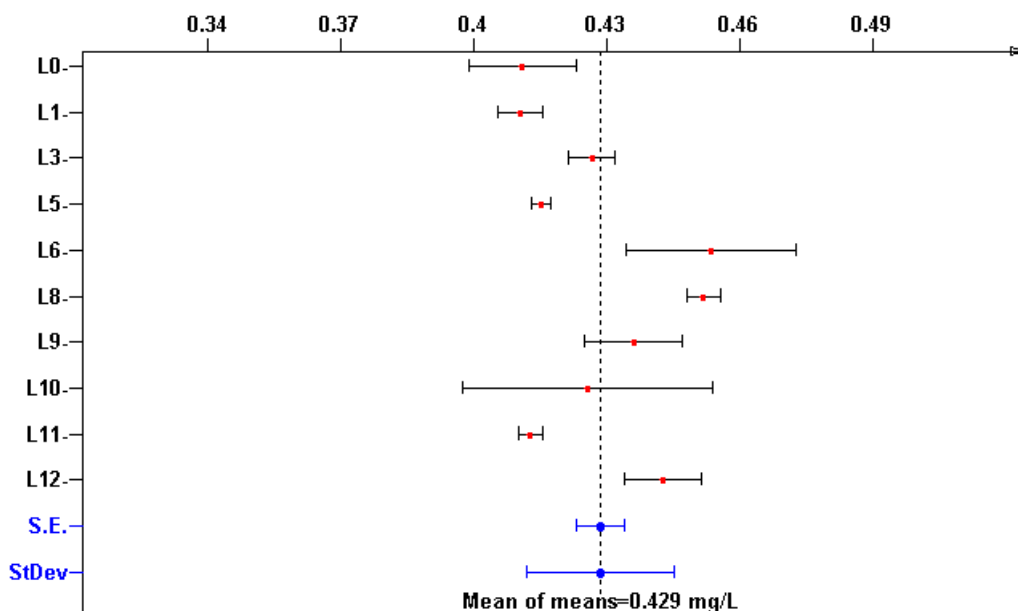
The bars in the graphs represent *s*, standard deviation of the measurement results. The X axis range covers approximately ± 20 % of the mean.

Ammonium

lab code	Replicates [mg/L]						mean	<i>s</i>
L0	0.418	0.425	0.421	0.401	0.406	0.395	0.411	0.012
L1	0.412	0.403	0.415	0.407	0.41	0.416	0.411	0.005
L2*	<i>0.62</i>	<i>0.64</i>	<i>0.55</i>	<i>0.64</i>	<i>0.54</i>	<i>0.62</i>	<i>0.602</i>	<i>0.045</i>
L3	0.42	0.43	0.43	0.43	0.42	0.43	0.427	0.005
L4*	<i>0.602</i>	<i>0.499</i>	<i>0.625</i>	<i>0.571</i>	<i>0.551</i>	<i>0.535</i>	<i>0.564</i>	<i>0.046</i>
L5	0.413	0.414	0.415	0.414	0.419	0.416	0.415	0.002
L6	0.477	0.429	0.444	0.438	0.468	0.465	0.454	0.019
L8	0.45	0.45	0.446	0.454	0.455	0.456	0.452	0.004
L9	0.445	0.439	0.45	0.431	0.433	0.419	0.436	0.011
L10	0.44	0.461	0.389	0.395	0.429	0.44	0.426	0.028
L11	0.414	0.414	0.41	0.417	0.411	0.411	0.413	0.003
L12	0.45	0.45	0.449	0.436	0.443	0.429	0.443	0.009

*datasets obtained by ion chromatography

Laboratory means and their standard deviations



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Title: Certification of the mass concentrations of calcium, chloride, magnesium, *ortho*-phosphate, potassium, sodium and of pH and conductivity in groundwater

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Abstract

This report presents the preparation and certification of the groundwater certified reference material ERM-CA616. All the steps required for the production of this water-matrix certified reference material are described in detail, from the sampling of natural groundwater until the characterisation exercise that lead to the final assignment of the certified values, following ISO Guide 34:2009 [1] and ISO Guide 35:2006 [2].

Homogeneity and stability of the water material were investigated with dedicated studies and the certification campaign for the material characterisation was based on an inter-comparison among several experienced laboratories. IRMM organised and coordinated all the phases of this project and carried out the evaluation of data.

The certified values were calculated as the unweighted mean of the laboratory means of the accepted sets of results for each parameter, see below. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) [3]. The stated expanded uncertainties include contributions from characterisation, homogeneity and stability.

GROUNDWATER		
	Mass Concentration	
	Certified value ¹⁾ [mg/L]	Uncertainty ²⁾ [mg/L]
Calcium	42.6	1.4
Chloride	44.6	0.9
Magnesium	10.1	0.3
<i>Ortho</i> -phosphate	2.24	0.10
Potassium	5.79	0.15
Sodium	27.9	0.8
	Electrochemical property	
	Certified value ¹⁾ [μS/cm]	Uncertainty ²⁾ [μS/cm]
Conductivity (20 °C)	426	5
	Chemical property	
	Certified value ¹⁾	Uncertainty ²⁾
pH (20 °C)	7.12	0.18
1) Unweighted mean value of the means of accepted sets of data each set being obtained in a different laboratory and/or with a different method of determination. The certified values and their uncertainties are traceable to the International System of Units (SI). 2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM, ISO/IEC Guide 98-3:2008) with a coverage factor $k = 2$, corresponding to a level of confidence of about 95 %.		

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